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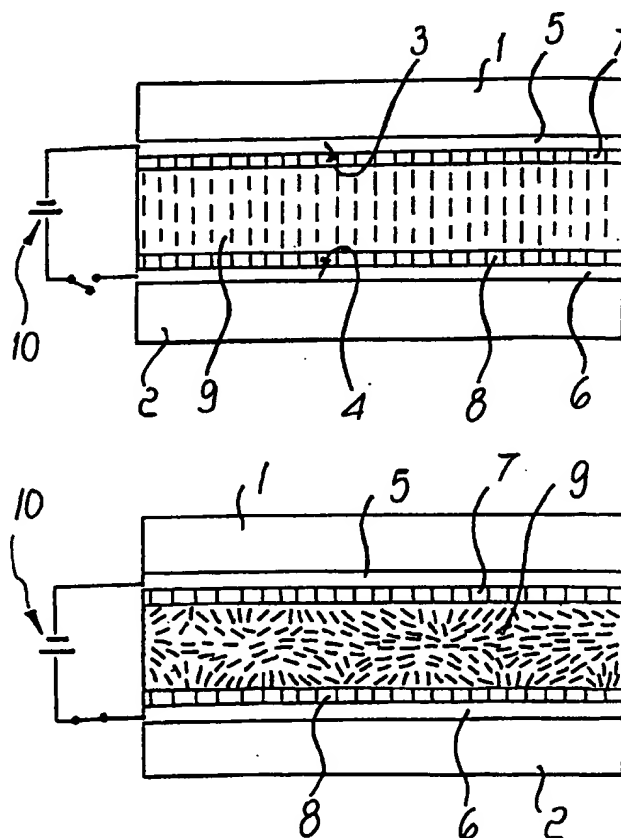


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP97/05598 <b>(22) International Filing Date:</b> 10 October 1997 (10.10.97) <b>(30) Priority Data:</b> PD96A000248 14 October 1996 (14.10.96) IT <b>(71) Applicant (for all designated States except US):</b> S.P.S. S.P.A. [IT/IT]; Via Enrico Mattei, 1, I-35046 Saletto (IT). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CHIDICHIMO, Giuseppe [IT/IT]; Contrada Bagno, I-87036 Rende (IT). DE FILIPO, Giovanni [IT/IT]; Contrada Baldanza, 5, I-87010 Do- ria-Cassano Ionio (IT). <b>(74) Agent:</b> MODIANO, Guido; Modiano & Associati, Via Merav- igli, 16, I-20123 Milan (IT).		<b>(81) Designated States:</b> AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>

**(54) Title:** LIQUID CRYSTAL DISPLAY DEVICE**(57) Abstract**

A display device comprising a flat or slightly hollow cell in which a thin layer of liquid crystals with negative dielectric anisotropy is interposed in a sandwich-like fashion between two transparent supporting layers made of glass or plastics whose faces, on the side of the liquid crystals, are rendered electrically conducting and are covered by a layer of a polymer having special characteristics, with a highly fractured surface divided into islands. In the absence of an electrical field, the liquid crystals are aligned, in a uniformly homeotropic manner, at right angles to the surfaces of the supporting layers polymeric coating and the cell is in a highly transparent state which is almost entirely independent of the viewing angle. By applying, through the conducting layers, an electrical field which is constant or variable over time with suitable frequencies and intensities, in the liquid crystals a division into microdomains with different orientation directions is obtained which produces a highly opaque state in the cell for visible light.



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## LIQUID CRYSTAL DISPLAY DEVICE

Technical Field

The present invention relates to a scattering liquid crystal display device, particularly suitable for application as a display, or as variable-transmission glazing, for various uses, in the field of motor vehicle components (rear-view mirrors, sun visors, etcetera) and in the field of building.

Background Art

The first display or electro-optical visual display unit in widespread use that used liquid crystal materials was the so-called Dynamic Scattering Mode (DSM) Liquid-Crystal Display, constituted by a liquid crystal display device with dynamic scattering mode.

This device is treated extensively for example in the following documents:

(1) Heilmeyer, G., Zanoni, L.A. and Barton, L.A., Proc. I.E.E.E., 56:1162 (1968).

(2) Bahadur, B. Dynamic Scattering Mode LCDs, in Liquid Crystals: Applications and Uses, Vol, 1, Ch. 9, ed. Bahadur, World Scientific Press (1990).

A class of display devices was developed from this first device which uses a high scattering state induced in a thin layer of liquid crystals by the combined effect of electrical fields applied to the cells and of ionic currents which are produced by said electrical fields and flow through the molecules of the liquid crystals.

The physical properties of liquid crystal materials used in these devices must be the following:

-- negative dielectric anisotropy;

- positive electrical conductivity anisotropy;
- electrical resistivity below  $10^{-10}$  ohm/m.

Figure 1 schematically illustrates these conventional devices.

5        It is clearly shown that the cell of the device does not use polarizers, since it is constituted only by conducting glass supports, plus one layer, approximately 20 microns thick, of liquid crystals combined with a reflecting mirror.

10       A cell of these devices has a very unusual electro-optical character.

At low voltage, typically 1 volt, the mesogenic liquid-crystal molecules are aligned at right angles to the electrical field, since they have a negative dielectric  
15       anisotropy.

If the cell is viewed in this condition with a polarizing microscope, the presence is observed of a uniform luminous field.

When the voltage is increased above 5 volts, an  
20       alternation of luminous and dark bands is observed owing to the onset of periodic alignment defects which have been termed Williams domains.

Figure 2 is a typical photomicrograph of Williams domains.

25       It is generally thought that Williams domains are generated by the looping of the so-called "nematic director", which is induced by the combined effect of the electrical field and of the ionic currents, as shown in figure 3.

30       A strong correlation is also noted between the

threshold voltage for the onset of Williams domains and the frequency of the applied field.

Two different frequency states can be observed; these states are separated by a cutoff frequency, above which  
5 (dielectric state) the Williams domains are replaced by another unstable configuration known as Chevron pattern.

Below the cutoff frequency (conducting state), the Williams regular configurations become unstable at twice the value of the threshold voltage and the device enters a  
10 dynamic scattering state.

It should be noted that optical contrast in these devices remains almost constant above the direct-current voltage at which the device enters the dynamic scattering mode, as shown in figure 4.

15 In the state of maximum transparency of the device, light transmission decreases rather drastically as the viewing angle increases (high haze).

This limits considerably the range of the applications in which it is most of all necessary that the device be  
20 transparent for very wide viewing angles, since the haze effect makes reading difficult during use as a display for data and/or information.

Moreover, DSM LCD devices, owing to the ionic currents, use considerable power during their operation and are not  
25 suitable for multiplexing applications.

Other electro-optical devices which are still in widespread use are so-called Twisted Nematic-Liquid Crystal Displays (TN-LCD), and are treated in:

(3) Schadt M., Helfrich W.: "Voltage-dependent optical  
30 activity of a twisted nematic liquid crystal", Appl. Phys.

Lett. 18, 127-128 (1971).

(4) Scheffer T.J., Nehring J.: "A new, highly multiplexable liquid crystal display", Appl. Phys. Lett. 45, 1021-1023 (1984).

- 5 (5) Scheffer T.J., Nehring J.: "Twisted nematic and supertwisted nematic mode LCDs" cap. 10 in LIQUID CRYSTALS - Application and uses - Ed. B. Bahadur World Scientific Singapore 1990.

In its simplest version, a TN cell comprises a layer of  
10 nematic liquid crystal enclosed between two electrodes made of transparent and conducting flat glass and kept at a constant distance by suitable spacers (between 5 and 10  $\mu\text{m}$  thick).

The liquid crystal has positive dielectric anisotropy.

- 15 Between the metallization of the electrode and the liquid crystal layer there is provided, on each electrode, a transparent alignment layer constituted by polymeric material.

By means of suitable abrasive rollers it is possible to  
20 generate microgrooves on said layer (this process is known as rubbing).

The alignment mechanism in these structures is still unclear: separate theories claim a simply elastic effect (caused by the shape of the microgrooves) or a chemical  
25 bonding effect (caused by the phase change due to surface melting when the groove is formed).

During the production of the TN-LCD cell, the electrodes are coupled so that the alignment directions are at  $90^\circ$  to each other, thus inducing a characteristic  
30 "helical" (twisted) configuration of the nematic liquid

crystal molecules that are present in the bulk of the lamina.

The cell is completed by two polarizing sheets whose polarization axes coincide with said alignment directions.

5        If no voltage is applied to the electrodes, the cell appears to be transparent, since the twisted structure induces a  $90^\circ$  phase shift in the polarization state which is equal to the phase shift between the polarization axes of said sheets.

10       In the presence of a voltage at the electrodes, the liquid crystal molecules instead tend to be orientated uniformly in the direction of the applied electrical field: the incoming polarized light no longer changes its polarization state and the cell appears dark.

15       Other conventional liquid crystal display devices entail, for their operation, one or two polarizing laminae for the light, in order to allow the device to be transparent if no power is supplied (reverse mode).

20       The polarizing films or laminae, however, are a filter for the light and reduce light transmission in the visible spectrum by as much as 40%.

This is highly negative, since it limits the possibility of "contrast", which is essential for good reading of a display in critical lighting conditions.

25       In high-luminance conditions (sunlight), only high contrast can make a display legible.

The industrial cost of the product is considerably affected by the polarizing laminae and, to a lesser extent, by the rubbing process.

Disclosure of the Invention



The aim of the present invention is to provide a liquid crystal display device of the reverse mode type which is transparent by virtue of intrinsic characteristics in the absence of an electrical field.

5        Within the scope of this aim, an object of the present invention is to eliminate the problems linked to the use of polarizers.

10       Another object of the present invention is to provide a liquid crystal display which allows to achieve high contrast.

Another object of the present invention is to reduce costs due to the use of polarizing laminae and to the rubbing process.

15       Another object of the present invention is to provide a liquid crystal display which can be manufactured industrially.

20       This aim, these objects and others which will become apparent hereinafter are achieved by a light scattering liquid crystal display device, characterized in that it is constituted by a cell composed of two transparent supporting layers between which a thin layer of liquid crystals with negative dielectric anisotropy is interposed, the internal faces of said layers (on the side of the liquid crystals) being rendered electrically conducting and being covered by  
25       a layer of a polymer having a highly fractured surface, which induces a mechanical orientation of the liquid crystal molecules, in the absence of an electrical field, at right angles to the supports, thus producing good transparency of the cell, while when a voltage is applied across the  
30       conducting layers the liquid crystal molecules with negative

dielectric anisotropy tend to be arranged unevenly at right angles to the field, with a "random" orientation on the plane parallel to the support, and are contrasted in doing so by the orientating action of the supporting surface, producing a considerable light scattering which is typical of an opaque state.

#### Brief Description of the Drawings

Further characteristics and advantages of the present invention will become apparent from the following detailed description of an embodiment thereof, accompanied by examples, which is given by way of non-limitative indication by using the accompanying drawings both to clarify the state of the art and to illustrate the new device, wherein:

figure 1 is a schematic view of a liquid crystal device of the DSM type;

figure 2 is a photomicrograph, taken with an optical polarizer microscope, illustrating Williams domains;

figure 3 is a view of the combined effect of the electrical field and of the ionic currents in a DSM device;

figure 4 is a view of a dynamic scattering condition in a conventional device;

figure 5 is a schematic view of the new device according to the invention, in the absence of an electrical field;

figure 6 is a schematic view of the new device in the presence of an electrical field in an opaque scattering condition;

figure 7 plots the electro-optical response of the device as a function of the applied field;

figure 8 plots optical transmissivity in the

transparent and opaque states, as a function of the viewing angle;

figure 9 is a photomicrograph, taken with an atomic-force microscope, of the fractured polymeric coating;

5 figure 10 is a photomicrograph, taken with an atomic-force microscope, of the layer of electrically conducting oxide.

#### Ways of carrying out the Invention

The device according to the present invention, as shown in figure 5, is composed of two external supporting laminae 10 1 and 2 made of transparent glass or plastics (for example PET) which are coated, on their inner faces, respectively 3 and 4, with transparent single or multiple electrically conducting layers 5 and 6.

The two electrically conducting layers 5 and 6 are 15 provided, for example, with indium tin oxide and a multilayer of silver tin oxide, with silver niobium oxide or with equivalent materials.

Two layers 7 and 8 of a polymer are coated on said conducting layers 5 and 6 and have a highly irregular and 20 fractured surface with a morphology constituted by mutually separated "islands".

In an optimum configuration, said islands have vertical dimensions between 1 and 10 nm and lateral dimensions between 10 nm and 1  $\mu\text{m}$ .

25 The surface fractures are due either to the surface fractures of the conducting oxide layer or to the surface fractures of the polymer layer or to the combination of the two configurations.

The two laminae 1 and 2 are coupled at a certain

distance so as to form an interspace 9 which is meant to contain the nematic liquid crystals with negative dielectric anisotropy.

The thickness of the interspace 9 is preferably between  
5 10 and 30 microns.

For the sake of clarity, an example of preparation and of components which can be easily applied industrially is given hereafter.

The two external supporting laminae 1 and 2 are made of  
10 glass, and indium tin oxide is used for the conducting layers 5 and 6; its surface morphology is shown in figure 10 in a photomicrograph taken with an atomic-force microscope.

A NISSAN SE-7511L polyimide was used for the surface coating layers, whilst a ZLI-4788-000 by Merck was used for  
15 the liquid crystal layer.

The coating was formed by dipping the glass laminae 1 and 2 in a solution of gamma-butyrolactone with 7% of the above-mentioned polyimide.

The glass was removed from the bath very slowly and  
20 drying was performed at 180° Celsius.

The preparation produced a highly fractured coating surface, as shown in figure 9.

Another example of preparation is described hereafter.

The two external supporting laminae 1 and 2 were made  
25 of glass, and an indium tin oxide was used for the conducting layers 5 and 6.

A NISSAN SE-7511 polyimide was used for the surface coating layers, while a ZLI-4788-000 by Merck was used for the liquid crystal layer.

30 The coating was formed with the spin-coating technique:

a few drops of a 6% solution of the above-mentioned polyimide in butyl Cellosolve (TM) were left on the glass laminae 1 and 2 and the laminae were spun at high speed (approximately 3000 rpm) for 2 minutes.

5       Drying was performed at 80° Celsius and curing was performed at 180° Celsius.

This method produces a high degree of fracturing of the surface coating.

10       The DC and AC electro-optical response at certain frequencies is plotted in figure 7 as a function of the applied supply voltage; it can be noted that light intensity in transparency depends on the voltage only at low frequencies.

15       The optical transmission characteristics in the transparent and opaque states are plotted in figure 8 as a function of the viewing angle.

Operation of the device is as follows.

20       In the absence of an electrical field, the liquid crystal molecules are oriented homeotropically and substantially uniformly at right angles to the supporting surfaces and the device has good transparency characteristics.

25       When a voltage of 10 volts (field equal to 0.4 V/ $\mu$ m) is applied across the two conducting layers, the liquid crystal molecules tend to be oriented at right angles to the field and are contrasted by the force caused by the surface, which would tend to keep them perpendicular to said surface and therefore parallel to the field. Since the coating, as mentioned, is not uniform because its surface is highly  
30       fractured into a plurality of islands, the ability of the

surface to contrast the orientation of the liquid crystal molecules is different from one island to the next of the polymeric coating. Accordingly, disorder in the orientation of the molecules occurs, causing the device to assume an  
5 intense scattering state which is typically opaque to visible light, as shown in figure 6.

A similar effect is achieved when alternating voltages are applied, but in this case the orientation disorder assumes a dynamic character, at least in the frequency range  
10 that the mesogenic molecules can follow with their orientating motion.

From the above description and from the illustrations it is evident that the intended aim and objects have been achieved and that in particular a device has been provided  
15 which has a reverse mode operation, using an innovative physical principle of competition between surface orientation and the orientation induced by the electrical field.

In this regard, the invention is different from the one  
20 related to devices of the DMS-LCS type described earlier, which use dynamic competition between the orientation forced by the electrical field and the disorientating effect of the ionic currents.

Attention is drawn to the advantage offered by the  
25 invented device, which in the absence of power supply for any reason is highly transparent due to intrinsic characteristics of the structure and of the components.

This transparency remains unchanged even at other viewing angles (haze free).

30 Another essential advantage is due to the lack of

light-polarizing laminae, which entails both savings in terms of cost and most of all higher efficiency in light transmission, which is not reduced by filters of this kind.

5 This entails very high efficiency, with the consequent possibility to have high contrast effects which are accordingly highly advantageous in any ambient lighting condition.

10 The component materials may obviously be chosen within a significant range, in compliance with the characteristics of the cited compounds, without thereby abandoning the scope of the protection of the present invention.

CLAIMS

1        1. A light scattering liquid crystal display device,  
2 characterized in that it is constituted by a cell composed  
3 of two transparent supporting laminae between which a thin  
4 layer of liquid crystals with negative dielectric anisotropy  
5 is interposed, the internal faces of said laminae (on the  
6 side of the liquid crystals) being rendered electrically  
7 conducting and being covered by a layer of a polymer having  
8 a highly fractured surface, which induces an orientation of  
9 the liquid crystal molecules, in the absence of an  
10 electrical field, at right angles to the laminae, thus  
11 producing good transparency of the cell, while when a  
12 voltage is applied across the conducting layers the liquid  
13 crystal molecules with negative dielectric anisotropy tend  
14 to be arranged unevenly at right angles to the field, with a  
15 "random" orientation on the plane parallel to the support,  
16 and are contrasted in doing so by the spatially uneven  
17 surface orientating action of the laminae, producing an  
18 intense light scattering which is typical of an opaque  
19 state.

1        2. A device according to claim 1, characterized in that  
2 said electrically conducting layer is provided by means of a  
3 single layer of metal oxide.

1        3. A device according to claim 1, characterized in that  
2 said electrically conducting layer is provided by means of a  
3 multilayer of metal and/or ceramic oxides.

1        4. A device according to claim 1, characterized in that  
2 said conducting layer is provided by means of a single layer  
3 of indium tin oxide or the like.



1        5. A device according to one or more of the preceding  
2 claims, characterized in that said conducting layer can be  
3 provided by means of silver tin oxide, tin oxide or  
4 equivalent compounds.

1        6. A device according to claim 1, characterized in that  
2 said fractured surface is caused by the surface fractures of  
3 the electrically conducting oxide layer.

1        7. A device according to claim 1, characterized in that  
2 said fractured surface is caused by the fractures of the  
3 polymer layer.

1        8. A device according to claim 1, characterized in that  
2 said fractured surface is caused by the combination of the  
3 surface fractures of the electrically conducting oxide layer  
4 and of the surface fractures of the polymer layer.

1        9. A device according to claim 1, characterized in that  
2 said fractures are constituted by islands with vertical  
3 dimensions between 1 and 100 nm and lateral dimensions  
4 between 10 nm and 1  $\mu\text{m}$ .

1        10. A device according to claim 1, characterized in  
2 that it uses any kind of liquid crystal having negative  
3 dielectric anisotropy.

1        11. A device according to claim 1, characterized in  
2 that the layer of said liquid crystals has a thickness  
3 between 10 and 30 microns or another thickness deemed more  
4 suitable to meet particular optical contrast requirements.

1        12. A device according to claim 1, characterized in  
2 that said polymer is a polyimide or any other kind of  
3 material, for example inorganic, having similar  
4 characteristics.

1        13. A device according to claim 1, characterized in

2 that said polymer is a mix of polyimides.

1 14. A device according to claim 1, characterized in  
2 that said polyimide is chosen among those that induce a  
3 homeotropic orientation or any other kind of material having  
4 similar orientating characteristics.

1 15. A light-scattering liquid crystal display device,  
2 characterized in that it uses liquid crystals with positive  
3 dielectric anisotropy and a polymeric coating which  
4 generates a planar orientation, with an operating mode based  
5 on the same kind of physical principle (competition between  
6 surface interaction and electrical field).

1 16. A light scattering liquid crystal display device,  
2 characterized in that it uses liquid crystals with positive  
3 or negative dielectric anisotropy and a polymeric coating  
4 which generates a tilted orientation, with an operating mode  
5 based on the same kind of physical principle (competition  
6 between surface interaction and electrical field).

1 17. A device according to one or more of the preceding  
2 claims, characterized in that said liquid crystals are mixed  
3 with inert spacers and/or coloring substances, gelling  
4 agents and/or any other kind of substance that can improve  
5 its characteristics or performance.

1 18. A device according to one or more of the preceding  
2 claims, characterized in that a layer of material is  
3 interposed between the metallic coating and the polymeric  
4 coating with the purpose of protecting the conducting layer  
5 against chemical corrosion and/or facilitate its adhesion  
6 with the polymeric layer.

1 19. A device according to claim 1, characterized in  
2 that one of the two supporting laminae is of the reflecting

3 or semireflecting type.

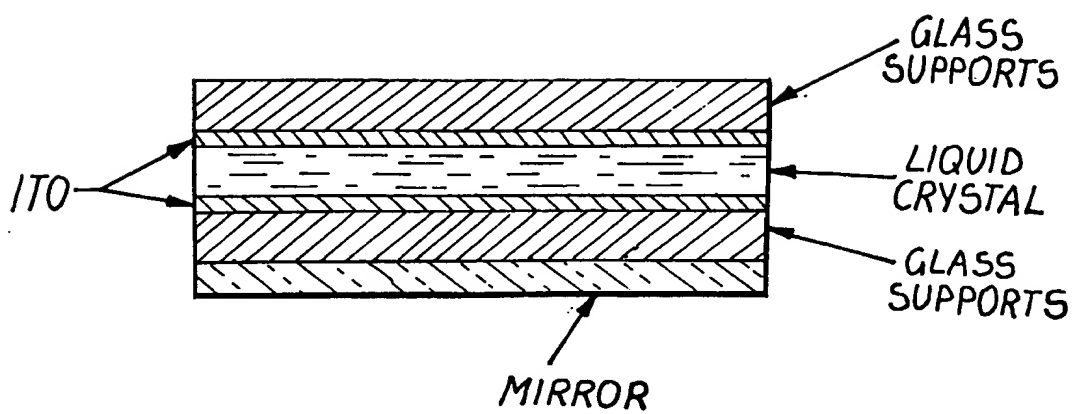
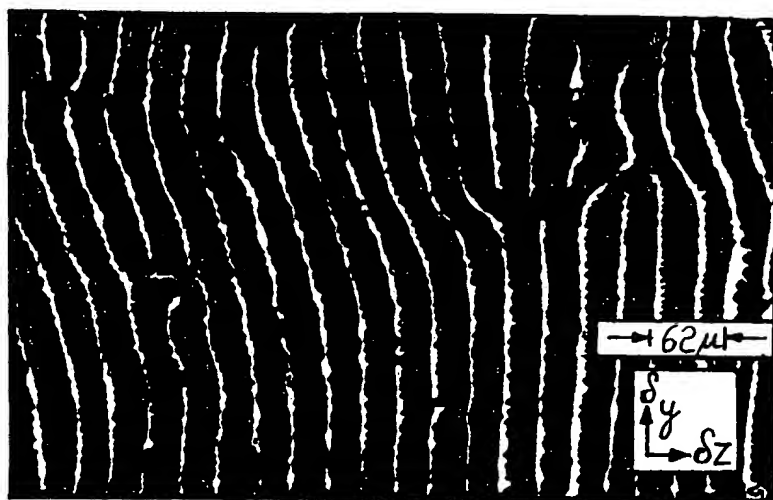
1       20. A device according to claim 1, characterized in  
2 that one of said supporting laminae is semitransparent.

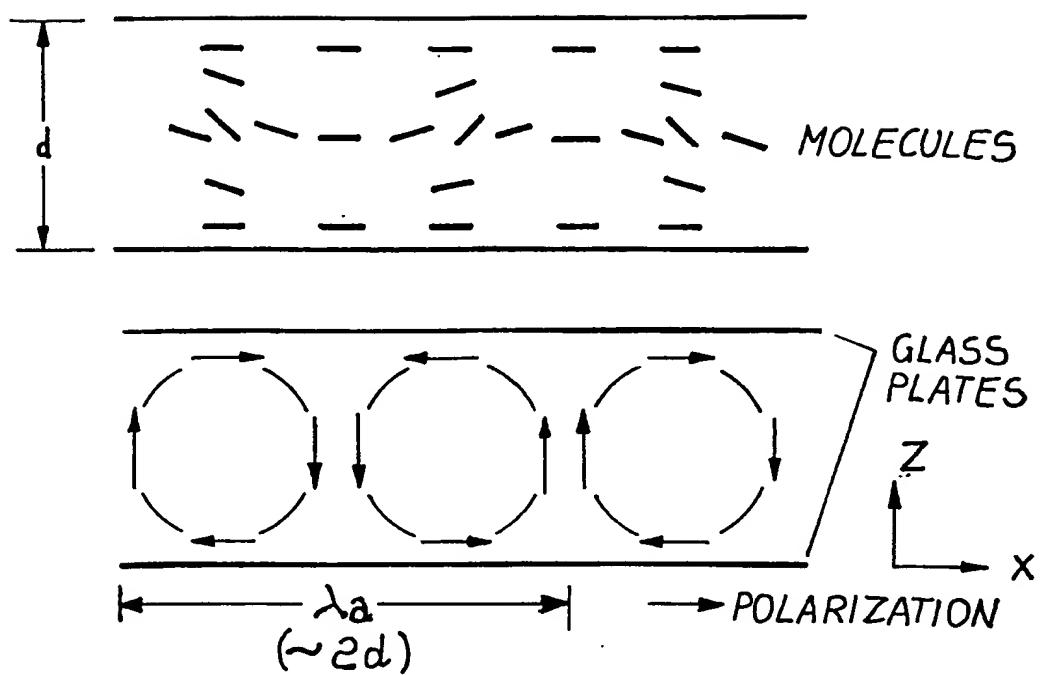
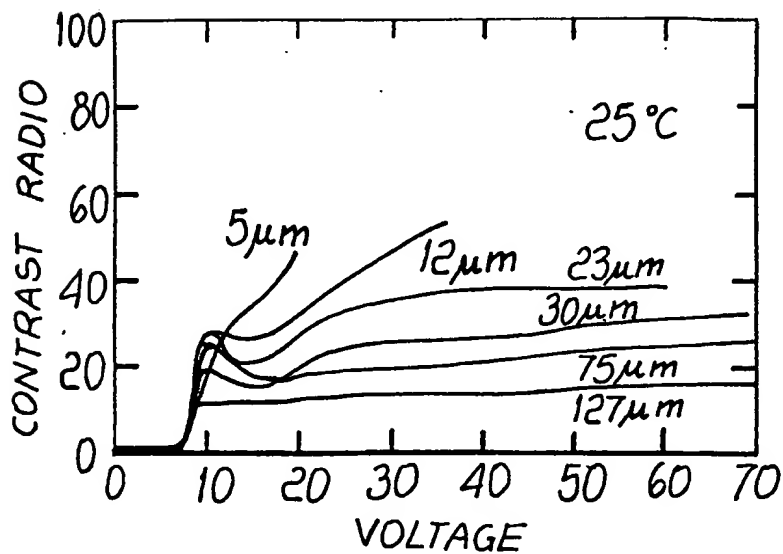
1       21. A device according to one or more of the preceding  
2 claims, characterized in that said supporting layers are  
3 made of rigid or flexible organic material and inorganic or  
4 composite material.

1       22. A device according to one or more of the preceding  
2 claims, characterized in that one or both of said supporting  
3 layers are made of, or comprise, a uniform or composite  
4 (organic or inorganic) material having suitable conducting  
5 and light-transmission properties.

1       23. An optical apparatus comprising, as a component, a  
2 liquid crystal device as defined in one or more of the  
3 preceding claims in addition to the necessary power supply  
4 and control instruments.

1       24. An apparatus according to claim 13, characterized  
2 in that said liquid crystal device acts as a display.

*Fig. 1**Fig. 2*

*Fig. 3**Fig. 4*

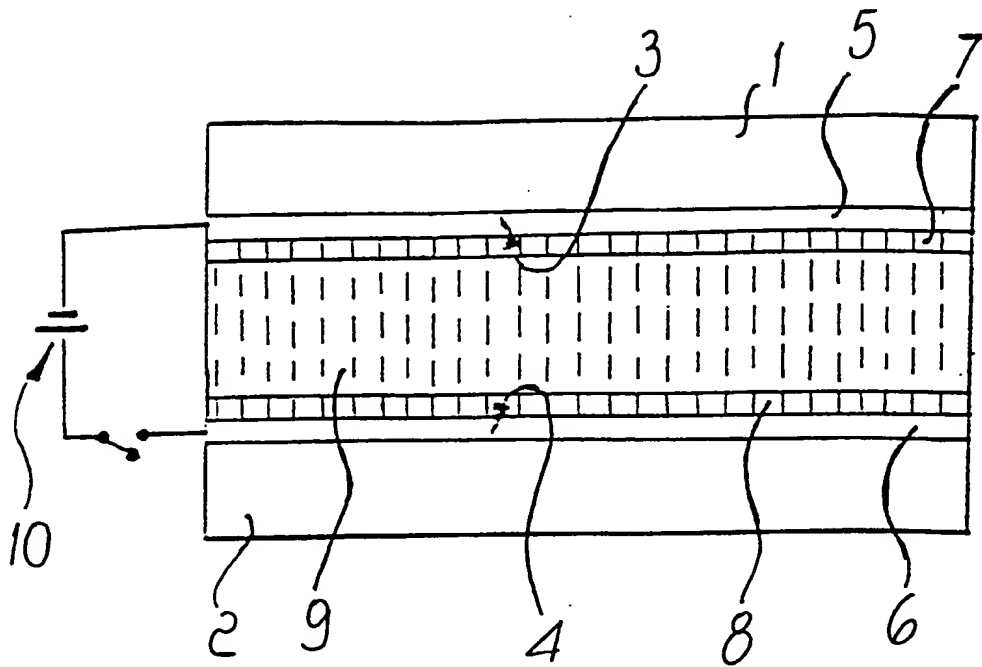


Fig. 5

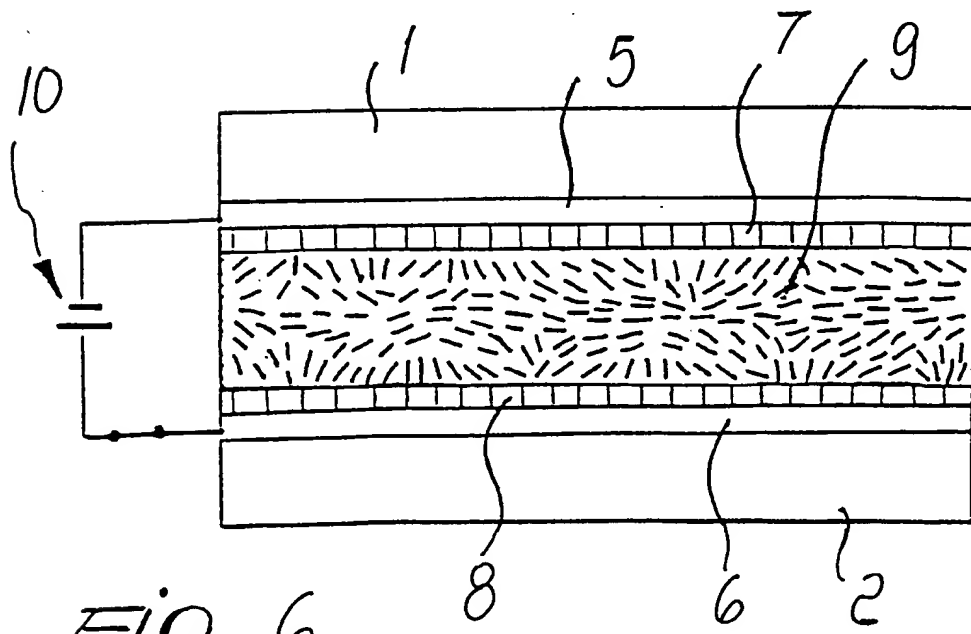


Fig. 6

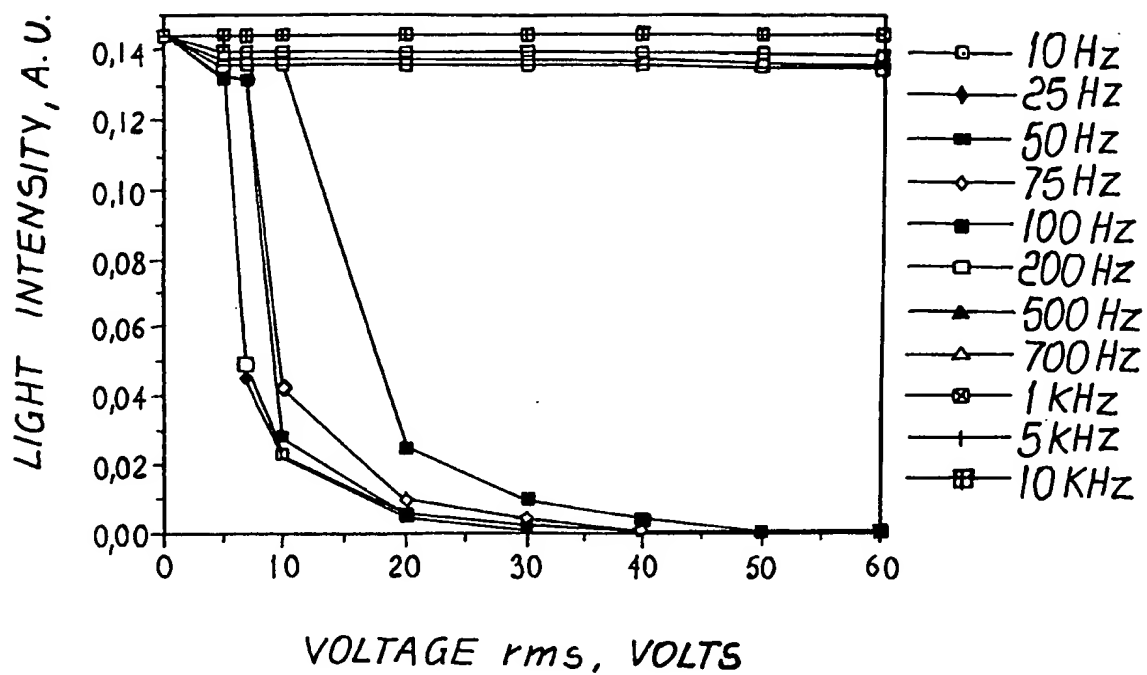


Fig. 7

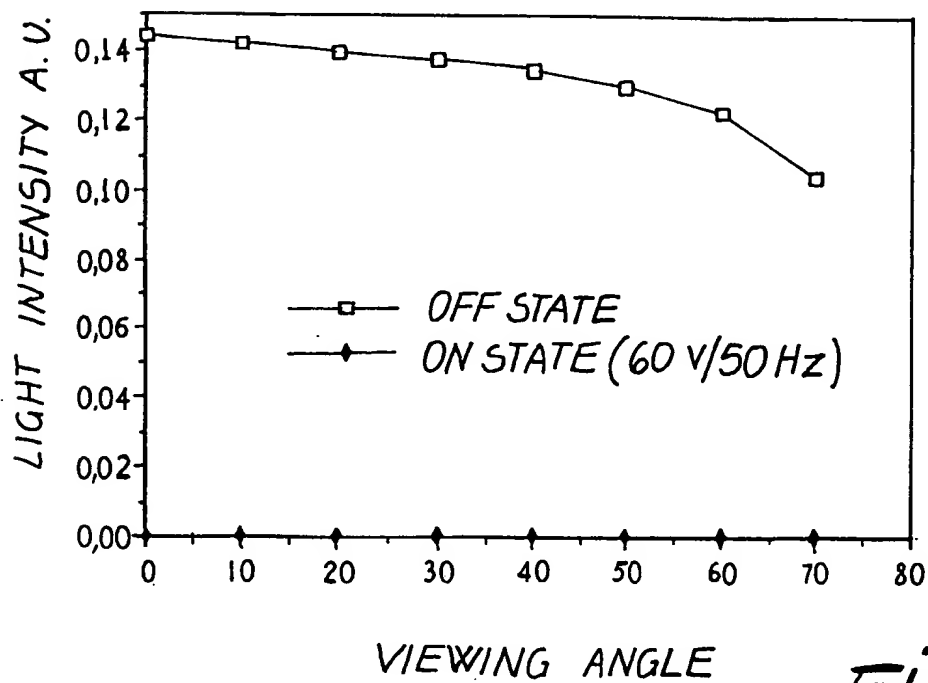
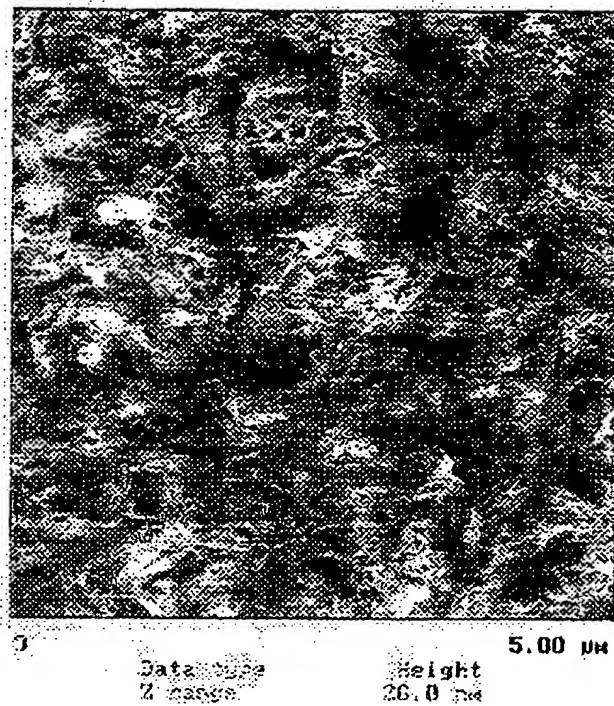
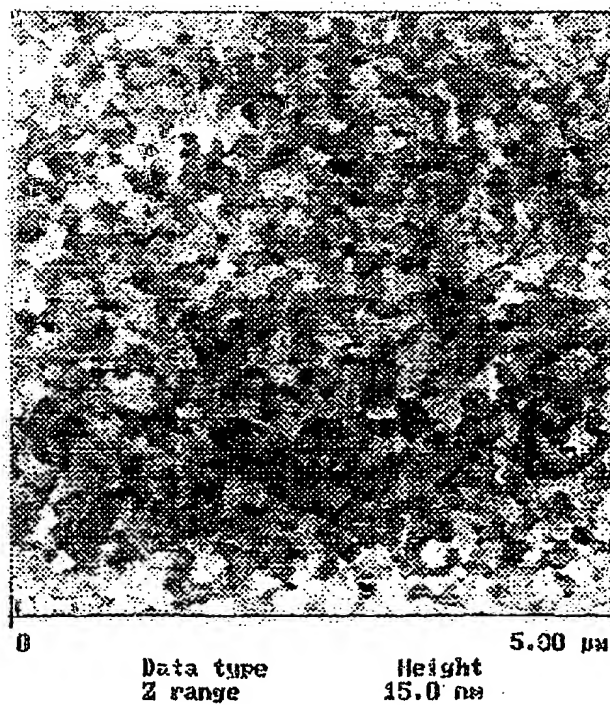


Fig. 8



*Fig. 9*



*Fig. 10*



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/05598

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G02F1/137 G02F1/1337

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 165 922 A (MORRISY JOSEPH H) 28 August 1979  see the whole document	1,2,4,5, 10-12, 14-16, 21-24
X	DATABASE WPI Section PQ, Week 9224 Derwent Publications Ltd., London, GB; Class P81, AN 92-200335 XP002055632 -& WO 92 09003 A (CHISSO CORP) , 29 May 1992 see abstract	1,2,4,5, 16,17, 19-24
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Date of the actual completion of the international search

13 February 1998

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/05598

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 526 (P-1617), 21 September 1993 - & JP 05 142515 A (RICOH CO LTD), 11 June 1993, see the whole document -----	15,16, 23,24
X	HIKMET R A M: "Electrically induced light scattering from anisotropic gels with negative dielectric anisotropy" MOLECULAR CRYSTALS AND LIQUID CRYSTALS, 1992, UK, vol. 213, ISSN 0026-8941, pages 117-131, XP002055574 see chapters "Introduction", "Experimental", "Conclusions" -----	1,2,4, 10,12, 14,16, 17,22-24

# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		FR 2350621 A	02-12-77